Charles University

Faculty of Science

Study programme: Chemistry

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Preparation of conjugated polymers-based fluorescence probes

Příprava fluorescenčních sond odvozených od konjugovaných polymerů

Bachelor´s thesis

Supervisor: RNDr. Jiří Zedník, PhD.

Prague, 2018

Statement

I hereby declare, that this bachelor thesis is my personal work and it was completed under guidance of my supervisor, RNDr. Jiří Zedník, PhD. at Charles University, Faculty of Science, Department of Physical and Macromolecular Chemistry and it has not been used in order to obtain any other academic degree.

Prague …….

Acknowledgments

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Last, but not least my deep thanks are dedicated to my family and friends, especially my parents, who believed in me and encouraged me through this time and in my life in general.

Abstract

The water soluble polythiophe–based polyelectrolytes, namely poly{3-[6-(triethylphosphonium) hexyl]-thiophene-2,5-diyl bromide} bearing the same ionic pendant groups but different in polymer main chain regioregularity 62 and 94% and molecular weight, respectively have been tested in order to study them as possible luminescent chemo-sensors. The fluorescent quenching with metals ions (Fe^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Cs^{+}, Co^{2+} and Ag^{+}) has been studied in water as a detailed survey. In order to continue and extend the study of various conjugated polymers as alternative luminescent sensors, luminescence quenching of poly(1-phenyl-1-hexyne) compound has been tested with nitrobeneze as a quenching agent. Final structure modification of model compound and preparation the phosphonium or ammonium based conjugated polyelectrolyte and consequent interaction with metal ions are planned for the future.

Bachelor thesis was done at Department of Physical and Macromolecular Chemistry at Faculty of Science at Charles University with the support of The Czech Science Foundation 17-05318S.

Abstrakt

Od polythiofenu odvozené polyelektrolyty (poly{3-[6-(triethylfosfonium)hexyl]-thiophen-2,5-diyl bromid}) byly studovány jako luminiscenční chemosensory. Zvolené polyelektrolyty nesly stejnou jontovou skupinu a lišily se regioregularitou polythiofenového hlavního řetězce (62 a 94 %) a molekulovou hmotností. Efektivita zhášení luminiscence byla detailně testována s ionty různých kovů (Fe^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Cs^{+}, Co^{2+} a Ag^{+}). S cílem prověřit další možnosti přípravy konjugovaných polyelektrolytů odvozených od polyacetylenu byl testován popsaný modelový polymer poly(1-fenyl-1-hexyn) a jeho interakce s nitrobenzenem. Finální strukturní modifikace modelové látky a následná příprava konjugovaných polyelektrolytů (amonium a fosfonium) jakož i interakce s modelovými kovovými ionty je plánována v nejbližší budoucnosti. Bakalářská práce byla vypracována na Katedře Fyzikální a Makromolekulární Chemie na Přírodovědecké fakultě Univerzity Karlovy s podporou grantu GAČR: 17-05318S.

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Abbreviations

CP	Conjugated polymers
ROMP	Ring opening metathesis polymerization
Pts	Polythiophenes
GRIM	Grignard metathesis polymerization
FRET	Fluorescence resonance energy transfer
NBS	*N*-Bromosuccinimide
P60	poly{3-[6-(bromo) hexyl]-thiophene-2,5-diyl} with 62% regioregularity
P90	poly{3-[6-(bromo) hexyl]-thiophene-2,5-diyl} with 94% regioregularity
P60-EtP$^+$	poly{3-[6-(triethylphosphonium) hexyl]-thiophene-2,5-diyl bromide} with 62% regioregularity
P90-EtP$^+$	poly{3-[6-(triethylphosphonium) hexyl]-thiophene-2,5-diyl bromide} with 94% regioregularity
SEC	size exclusion chromatography

1. Introduction

1.1 Conjugated polymers

Conjugated polymers (CP) attract interest of many researchers in the last few decades due to their potential usability in various areas of organic, inorganic or materials chemistry, biochemistry, photovoltaic cells[1–3], diagnostic devices[4], electronics[5], sensors[6,7], artificial muscles[8] and gas storage[9–11]. Conjugated polymers are characterized by alternating single and double bonds in their main-chain, allowing partial delocalisation of π – electrons along the backbone of the polymer chain. Various types of CP are known. The most studied are polyacetylenes, polyphenylvinylenes, polyanilines, polythiophenes and polyfluorenes. These types are shown in Figure 1.

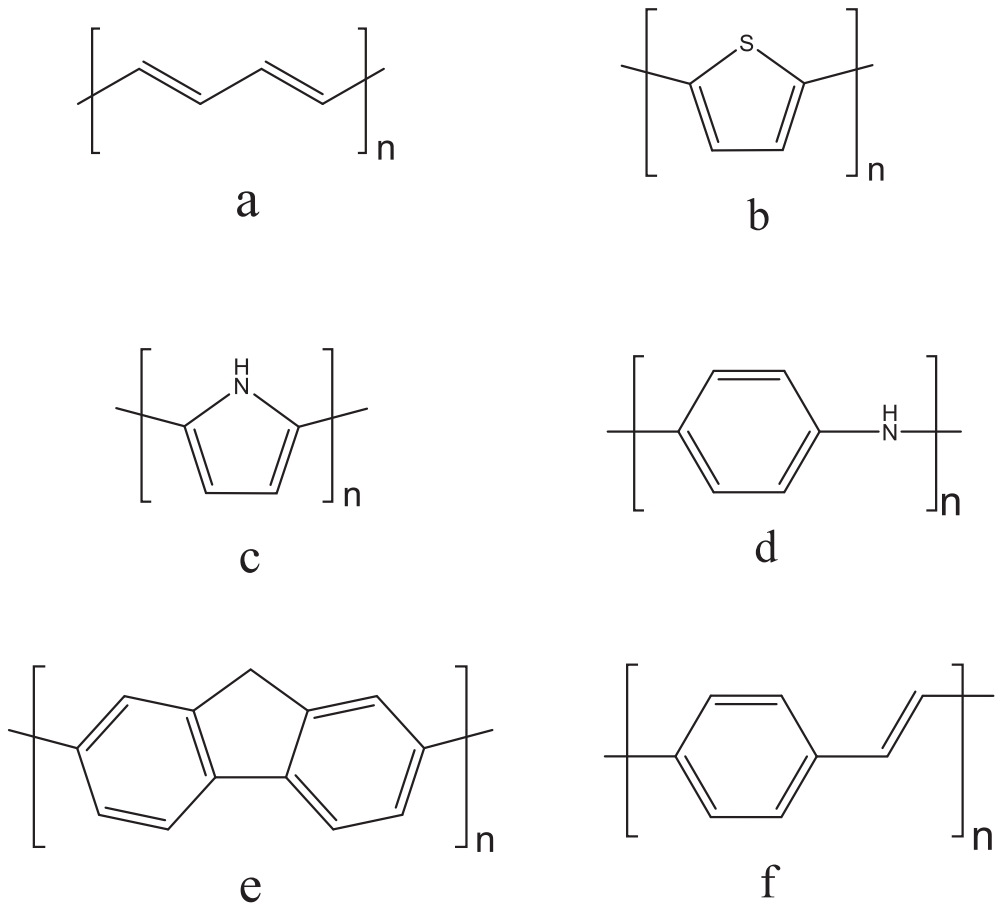


Figure 1: The most used conjugated polymers: *trans* - polyacetylene (a), polythiophene (b), polypyrrole (c), polyaniline (d), polyfluorene (e), polyphenylene vinylene (f).

Main breakthrough in the field of conjugated polymers has come with an accidental mistake made during acetylene polymerization by Ziegler – Natta catalyst in laboratory of professor Shirakawa. A much higher concentration of catalyst then usually was used in that reaction. Instead of powder material, the thin film was obtained, exhibiting interesting properties[12]. Subsequently, prof. A. G. MacDiarmid and prof A. Hegger studied this phenomenon, investigated it more deeply and reported in 1977 that "doping reaction" (the oxidation of polyacetylene with iodine) leads to the significant increase of the polyacetylene's conductivity[13] nearly to metallic level. All these three chemists were later awarded by the Nobel Prize in Chemistry in 2000 for this achievement[12,14]. Scientists were forced to search for new conjugated polymers because of low

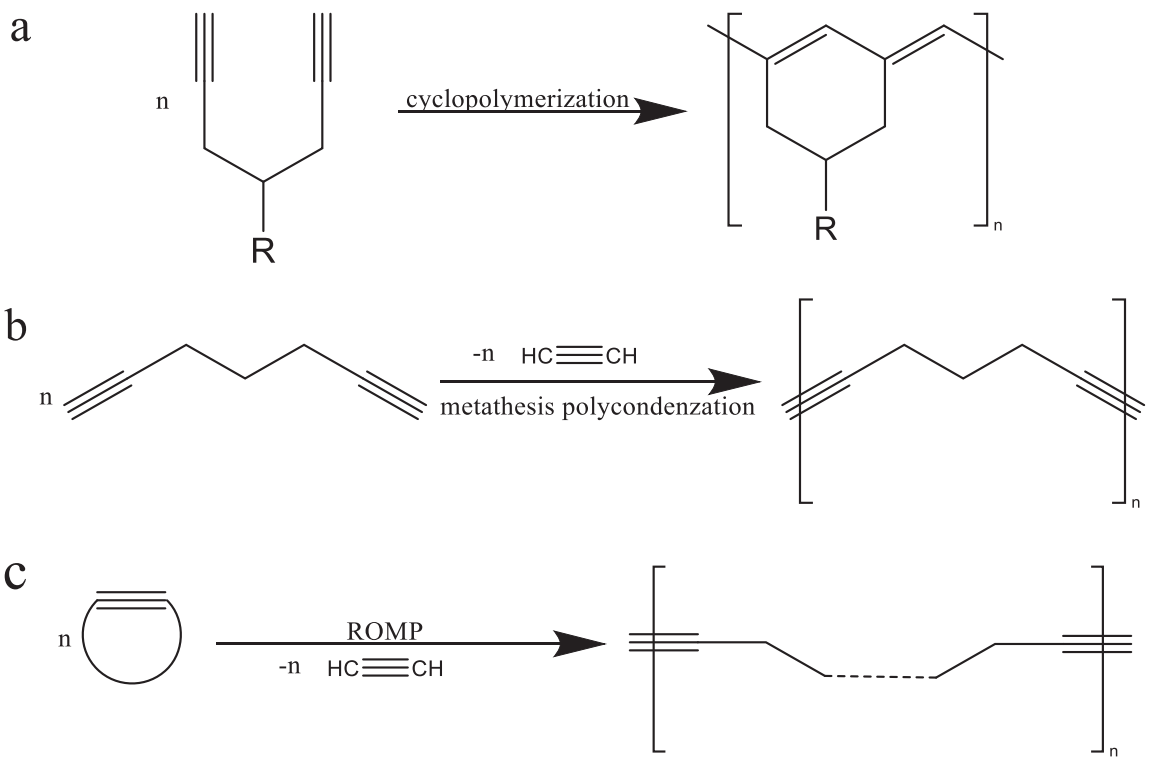
non-substituted polyacetylene‘s oxidative stability[15] and difficult processability[16,17]. Consequently new groups of conjugated polymers were synthesised, for example polypyroles[18], polyanilines[19,20], etc. Conjugated polymers have several advantages: low cost, good processability and flexibilility[21]. Their optoelectronic properties could be easily tuned. On the other hand, conjugated polymers suffer by various disadvantages, e.g. lack of charge carriers without doping[14]. Structure defects lead further to the decrease of charge carrier mobility.

Preparation of a conjugated polymer requires the various types of catalytic processes that often result in formation of such defects. A small amount of remaining catalyst influences properties of synthesized material and it decreases its performance in resulting optoelectronic devices[22]. Moreover, conjugated polymers are prone to an oxidation and deterioration from UV irradiation[23]. Conjugated polymers are less stable that their inorganic counterparts in general.

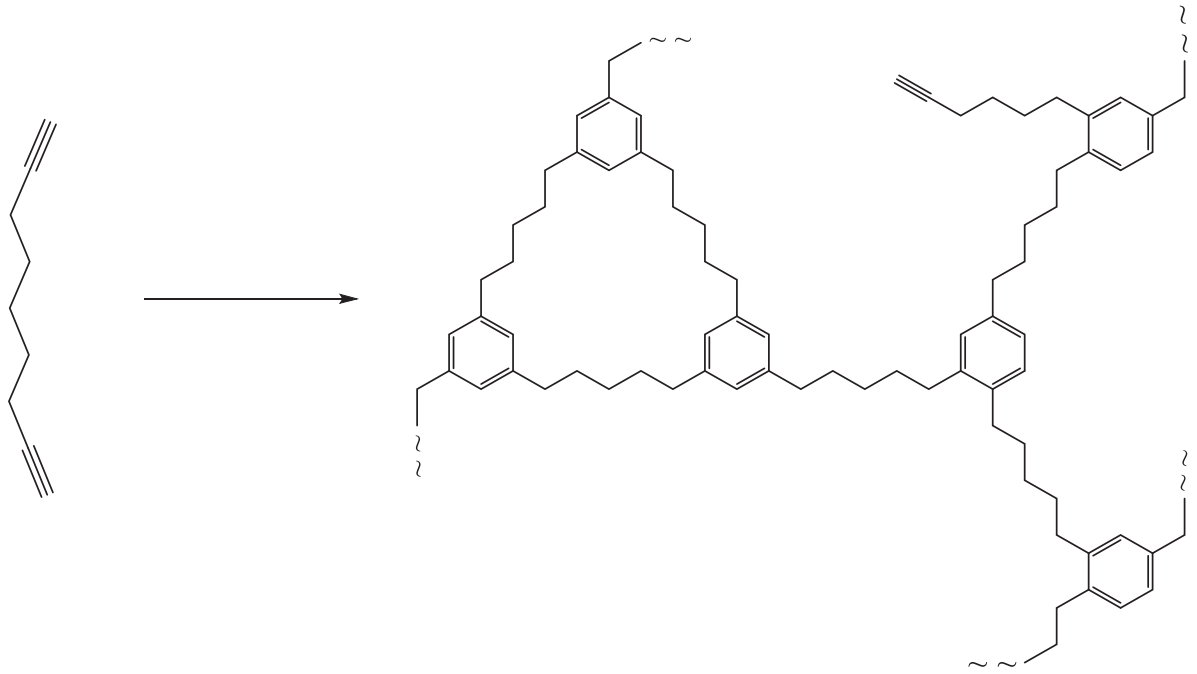
Polyacetylenes

Polyacetylenes are defined as polymers prepared from acetylene-based monomers by polymerization involving triple acetylene bond. The most known types give the chain skeleton of polyvinylene structure, where the main chain consist of linear sequence of alternating single and double bonds (conjugated double bonds)[24]. Presence of alternating single and double bonds is reason for excellent mobility of charged species along the polymer chain formed by doping reaction. Polyacetylenes are typically prepared by a chain – grow coordination polymerization. Catalysts work either by insertion mechanism (typically based on Rhodium)[25] or in metathesis mode[25]. Unfortunately, the majority of Grubbs or Shrock carbene Ruthenium or Molybdenum complexes appear as inactive in polyacetylene polymerization[26]. It is worth to mention, that recent reports describe a new generation of Shrock Molybdenum Carbenes exhibiting ability to polymerize acetylene-based monomers[27]. Another reaction is a ring opening metathesis polymerization (ROMP)[28], where the polymer is prepared from cycloalkynes preserving triple bonds[29], which does not necessarily leads to conjugated structures.

Also, some special type of acetylenic monomers reactions were described in the literature. Some special type of polyarylene forming polymerization may be cyclopolymerization[29], where a new circle within the monomeric unit is formed during the polymerization, and polycyclotrimerization based on 2+2+2 cyclotrimerization of monomers containing two or more triple bonds along with formation of benzene as knot point[30]. Mentioned type is usable for preparing polymer networks and was also used by our group[31]. All mentioned reactions are depicted in the schemes below.



Scheme 1: The scheme of cyclopolymerization (a), triple bond – preserving polymerization (b) and ring opening metathesis polymerization (c).



Scheme 2: Cyclopolymerization based on 2+2+2 cyclotrimerization of monomer containing triple bond.

Polythiophenes

Important subclass of conjugated polymers is represented also by conjugated polythiophenes (Pts). These materials have high charge carrier mobility (after doping), provide high absorption in the visible spectral range and offer various possibilities of tuning of their properties by changing of substituents on the main chain of polymer.

Firstly, professors Yamamoto and Lin synthesized polythiophene in 1980. They prepared unsubstituted polythiophene by oxidative polymerization of thiophene using $FeCl_3$[32,33]. Although the reaction was successful the product could not be processed, because of its insolubility. Soluble poly(3-alkylthiophenes) were prepared with use of Ni^{2+} metal polymerization catalyst few years later[34]. The side-groups attached on each monomeric unit are the reason for processability of overall polythiophene system due to partial twisting of mentioned units out of plane causing limitation of π- π stacking. Despite the fact, that the system is not planar, conjugation extent is still sufficient for the polymer usage. The mentioned side groups are responsible for asymmetry of monomeric thiophene units, which means they can vary in their steric hindrances based on the chain regioregularity. Ideally, the thiophenes units would be linked regularly by head-to-tail manner. In fact, also irregular linkages are present, namely head-to-head and tail-to-tail linkages[35]. Isomerism by regioregularity is shown in Figure 2.

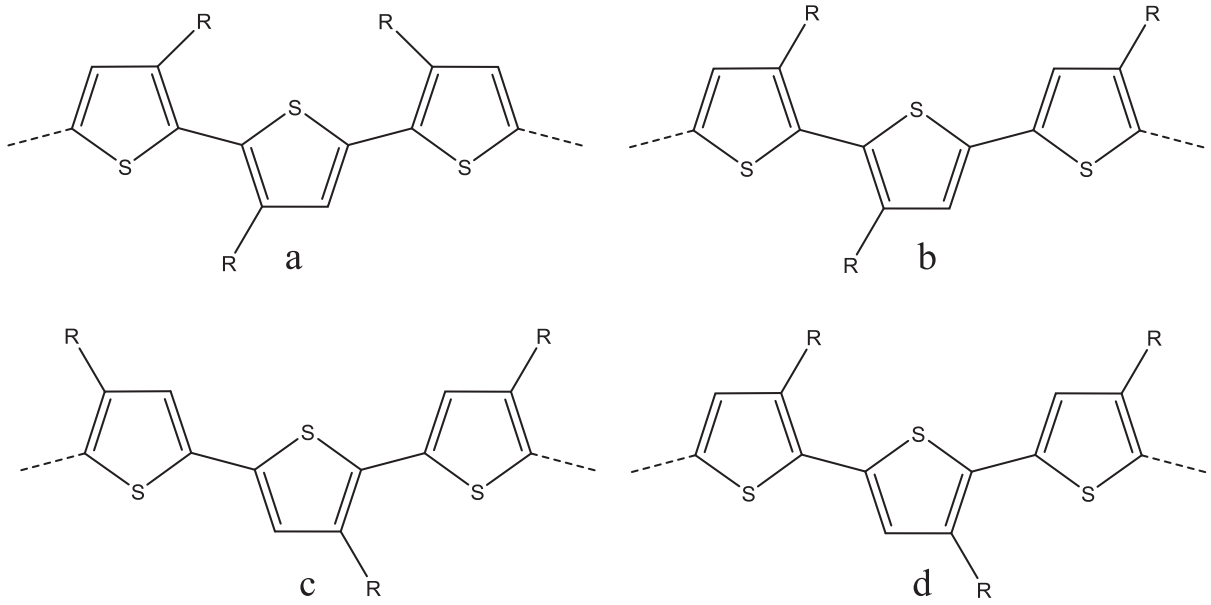
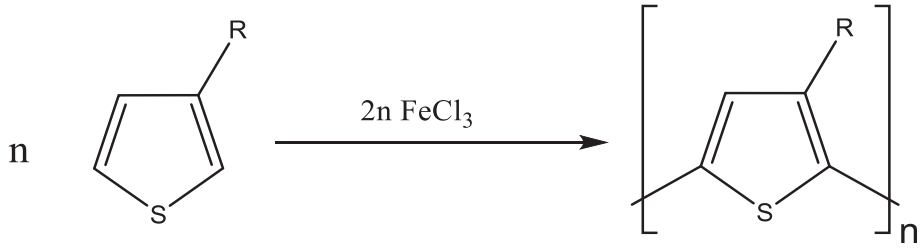


Figure 2: Types of regioregularity: head-to-head – tail-to-head (a), head-to-head – tail-to-tail(b), tail-to-tail – head-to-tail (c) and head-to-tail – head-to-tail (d).

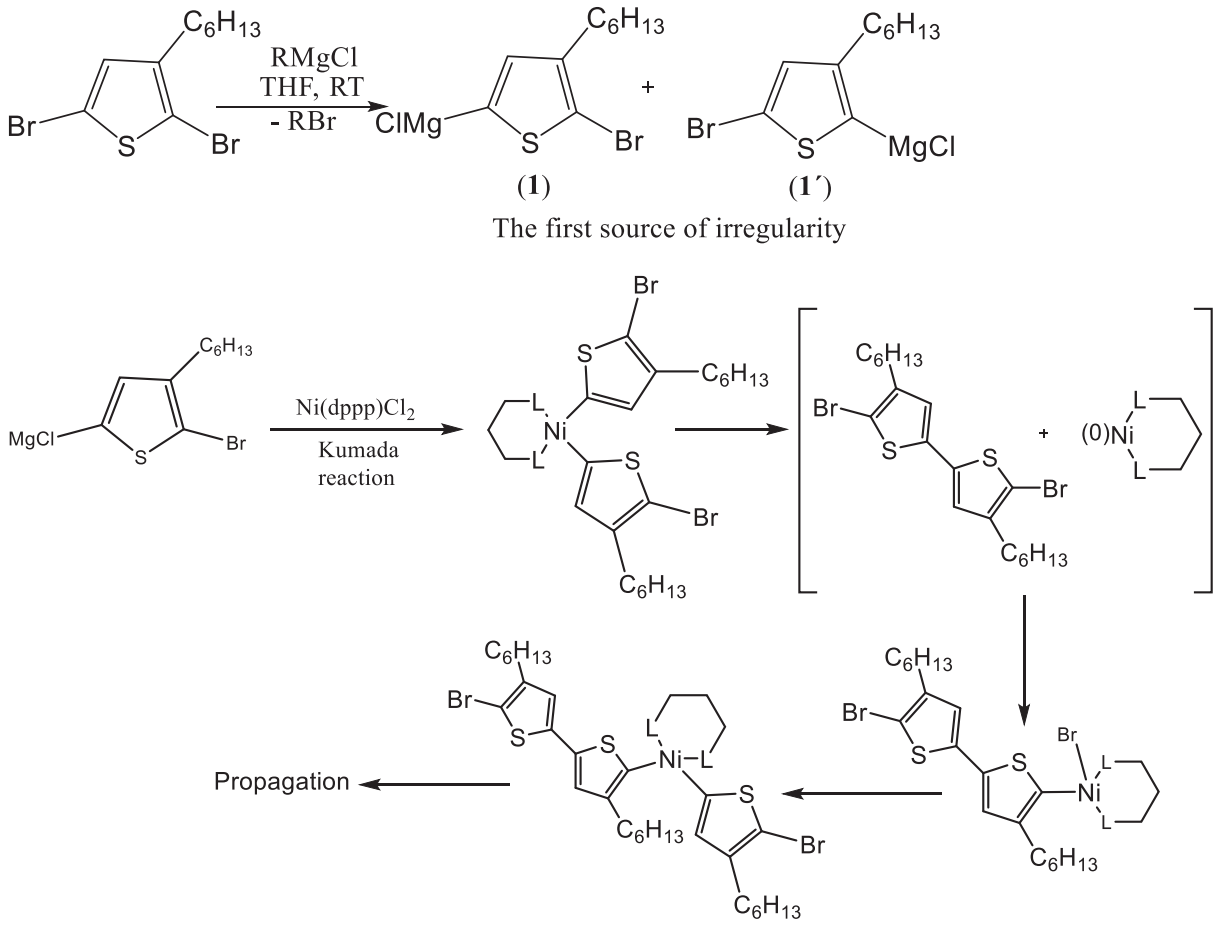
The simplest procedure of polythiophenes preparation is aforementioned oxidative polymerization of thiophene. Although, this process is quite simple the resulting head-to-tail regularity is usually low (about 50%), but it can be increased by decreasing the temperature of the reaction[36]. It means that prepared polymer is presumed as irregular. Also, this procedure usually does not lead to the preparation of high molecular weighted polymers. The process of oxidative polymerization of thiophene is shown in Scheme 3.



Scheme 3: The scheme of oxidative polymerization with $FeCl_3$ oxidative reagent.

Example representation of process leading to polymer with tailored properties (highly regioregular polymer) is known as the Grignard metathesis polymerization (GRIM). It was developed by McCullough and co-workers[37].

Although synthesis is presumed as routine, it is relatively difficult to perform due to its limited reproducibility. The inert atmosphere and dry reagents and environment are required. This procedure gives highly regioregular polythiophenes with up to 98% of head-to-tail connections of thiophenes units. Higher regioregularity could not be reached by the principle. Another possibility, which is worth to mention is the usage of Rieke Zinc[38]. Aforementioned high regularity causes polymer's better charge carrier mobility. The side chains of thiophene end-capped by bromide atoms do not influence the efficiency of the GRIM process. A highly regioregular poly[3-(6-bromohexyl)thiophene-2,5-diyl]s have been prepared by various researchers[39,40]. The presence of pedant bromide groups on the highly regioregular polythiophene conjugated main chains opens the possibility of various post-polymerization reactions. The presumed mechanism of Grignard metathesis polymerization is shown below.



Scheme 4: Proposed mechanism of Grignard metathesis polymerization[35].

Polyelectrolytes

Polyelectrolytes are important materials which consist of $\pi - \pi$ – conjugated main chain and a high content of ionic or ionizable side groups along the skeleton providing solubility in polar solvents (also in "green solvents" like water or alcohols)[41]. They are divided into two groups: anionic and cationic based on the charge of ionic pendant group. Polymers with ionic charged group located on the main-chains atoms are known as ionenes.

The most studied conjugated polyelectrolytes are bearing phosphate, carboxylate and sulfonate groups. One pathway for preparation of conjugated polyelectrolyte is based on modification of corresponding conjugated polymer precursors such as poly (phenylene vinylene), polyfluorene and poly (p-phenylene) carrying side groups–bearing reactive sites. Conjugated

polyelectrolytes have found applications in light-emitting diodes and photovoltaic devices[42,43]. Typical examples of water-soluble polyelectrolytes are 3-substituted polythiophenes, poly(phenylene vinylene), polyfluorene, etc[44,45].

Conjugated polyelectrolytes interact with oppositely charged substances. This feature opens possibility to develop various fluorescent-based sensors for proteins, DNA and biomolecules. In many cases, such interactions lead to the fluorescent quenching or “amplified quenching”[46]. The fluorescent resonance energy is transferred from conjugated backbone to negative or positive charged agent. The solubility of conjugated polyelectrolytes in aqueous media is reason why they are suitable for the development of biosensors in living organism.

1.2 Fluorescence

Luminescence is generally presumed as the emission of photon(s) from molecule in excited state. It is divided into two categories, depending on the electron spin in the excited state. These two categories are fluorescence and phosphorescence. The first type denoted as fluorescence occurs when excited electron relaxes to its ground state from singlet excited state. Typical lifetime of this process is within the range of nanoseconds. Phosphorescence possess longer lifetimes and excited electron relaxes from triplet state. The luminescence is commonly observed from fluids, thin films or particles. In some cases fluorescence and phosphorescence allows us to quantitative sensing of quenchers[47].

Quantum yield of fluorescence

After the excitation of electron, both the radiative and non-radiative processes are taking place. Luminescence quantum yield (ϕ_F) is defined by the ratio of the emitted photons to the number of absorbed. Possible formulation of this value is also by speed constants of these processes:

$$\phi_F = \frac{n_{\mathrm{F}}}{n_{\mathrm{A}}} = \frac{k_{\mathrm{F}}}{\sum_i k_i} \qquad (1)$$

where n_{A} is number of absorbed photons, n_{F} number of emitted by the fluorescence as result of absorption protons A, k_{F} is speed constant of fluorescence and $\sum_i k_i$ is representing all constants of emitting and non-emitting processes[48].

Fluorescent quenching and Stern-Volmer equation

There are various types of fluorescence quenching. The quenching can be caused either by formations of compounds (complex, aggregate, etc.) between the fluorophore and quencher, or in collision mode. Quenchers can also act by a fluorescence resonance energy transfer mechanism (FRET)[49]. For collision

quenching, chemical alteration is not present. Other mechanism of quenching can be static, where not-fluorescent complexes are formed by fluorophores, or can occur via many trivial processes such as decay of the excitation light by fluorophore or other absorbing species. The process when fluorescence of a certain fluorophore is reduced after adding a quencher is now commonly known as “dynamic fluorescent quenching”. Process of fluorescence quenching can be evaluated by a basic Stern-Volmer equations:

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q], \tag{2}$$

and

$$K_{sv} = k_q \tau_0 \tag{3}$$

where I_0 and I are the fluorescence intensities of fluorophore and the fluorophore quenched with certain amount of quencher, $[Q]$ is concentration of quencher, τ_0 is the natural fluorescence lifetime (with absence of quencher) of excited state, and k_q is specific constant describing bimolecular collision and its deactivation of electronic energy. The K_{sv} is Stern-Volmer constant[48].

2. Aims of thesis

- Examine luminescence quenching of previously prepared polyelectrolytes (poly{3-[6-(triethylphosphonium) hexyl]-thiophene-2,5-diyl bromide}) differing in regioregularity of the polymer main chain with various metal ions (Fe^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Cs^{+}, Co^{2+} and Ag^{+}), used as quenchers
- Determine sensing limits of selected quenchers
- Preparation of poly(1-phenyl-1-hexyne) and its interaction with nitrobenzene

3. Experimental Part

Chemicals

Methanol, tetrahydrofuran, chloroform and toluene were purchased from Sigma – Aldrich and dried or purified by standard methods. Toluene was distilled under argon from sodium/benzophenone before usage.

The 1-phenylhexyne was purchased from Sigma – Aldrich. WCl_6 and Ph_4Sn were used as received. Nitrobenzene was used after distillation under vacuum. Poly{3-[6-(triethylphosphonium)hexyl]-thiophene-2,5-diyl bromide}s were received as a kind gift from Dr. Sviatoslav Hladysh (see below).

UV/vis spectroscopy

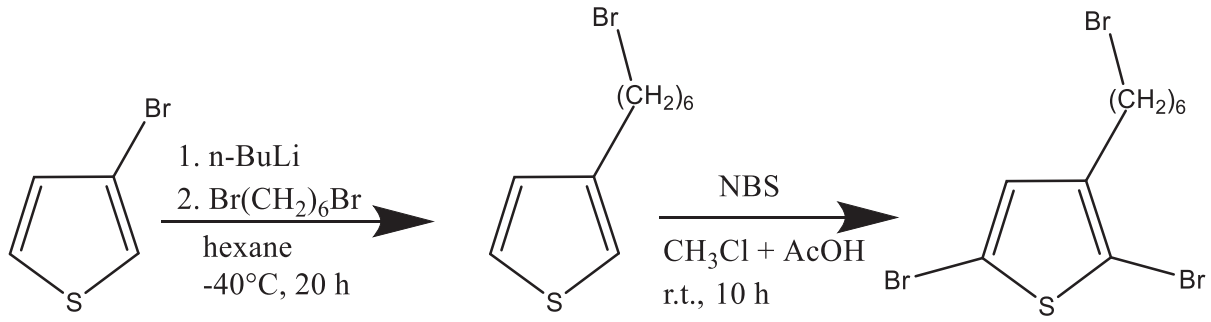
Used UV/vis spectra of studied polyelectrolytes used in current thesis were taken from published work[35]. Briefly: Spectra recorded on Shimadzu UV-2401PC using solvent mixture chloroform/methanol (1/1 by vol.) and water solutions of the prepared compounds.

Photoluminescence spectroscopy

Photoluminescence spectra were measured on a Fluorolog 3-22 Jobin Yvon Spex 3 instrument (Jobin Yvon Instruments S. A., Inc., USA) in solutions (see fluorescent measurements) using four-window quartz cuvette (1 cm). The emission spectra were excited using the wavelength, λ_{ex} (for **P60-EtP$^+$** and **P90-EtP$^+$** - 420 nm and for **Br11** - 325 nm) equal to the position of the absorption maxima of particular compound. Laser diode (378 nm) was used as an excitation source for time resolved measurements. Used concentrations are specified in each experiment (see below).

Synthesis

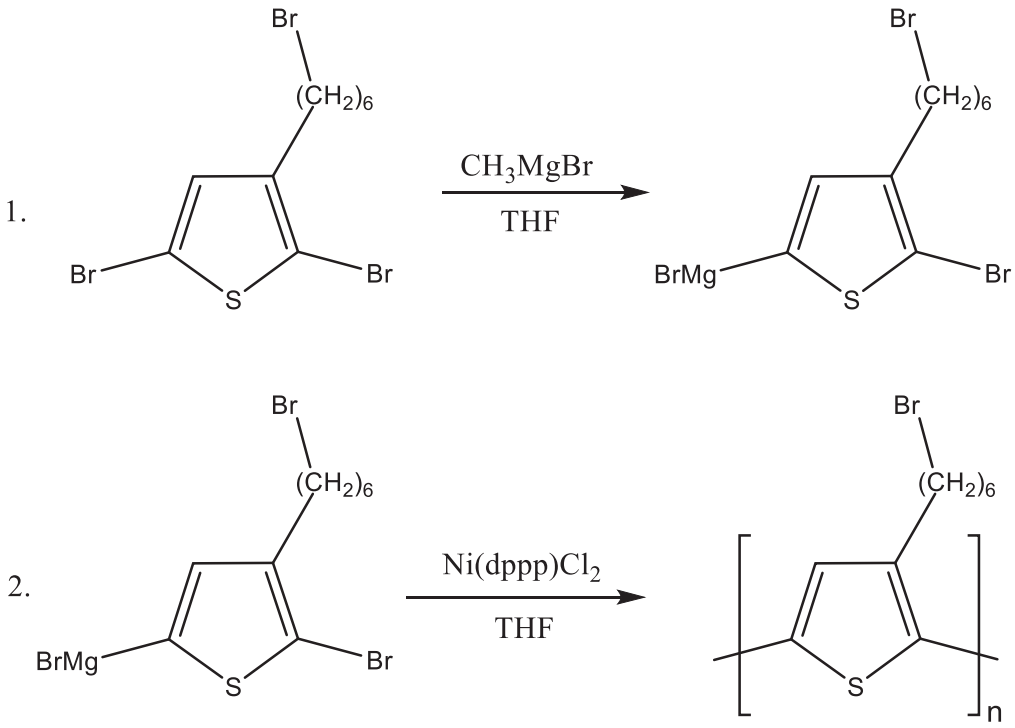
Polythiophene – based material



Scheme 5: Preparation of the monomer (2,5-dibromo-3-(6-bromohexyl)-thiophene).

Presented polythiophene polyelectrolytes with two different regioregularities, denoted as **P60-EtP$^+$** (polymer with regioregularity of 62%) and **P90-EtP$^+$** (polymer with regioregularity of 92%) were prepared previously and published by Dr. Sviatoslav Hladysh[39] and were received as a kind gift.

However, brief description of their synthesis is included into this work for better clarity. Firstly, starting monomer, 3-bromothiophene was mixed with *N*-butyllithium with following addition of 1,6-dibromohexane in dry hexane The reaction mixture was allowed to react at -40°C for 20 hours. It was then mixed with NBS (*N*-bromosuccinimide) in dichloromethane/ethanol solvent mixture at room temperature for 10 hours. The polymerization is briefly summarized in Scheme 6.

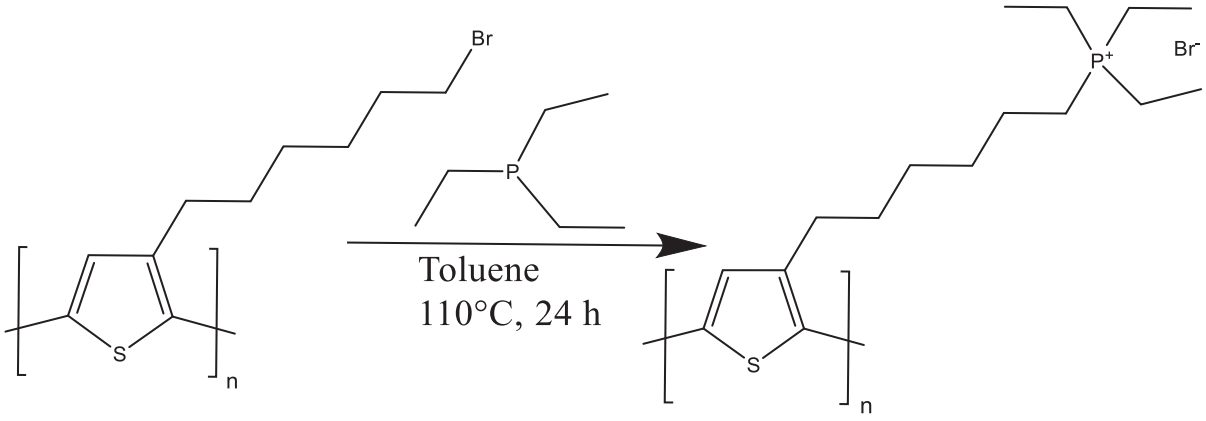


Scheme 6: Polymerization of 2,5-dibromide-3-bromohexylthiophene by Grignard metathesis polymerization.

The monomer was polymerized by Grignard metathesis polymerization. In order to obtain highly regioregular polymer (94%) (**P90**), temperature of polymerization was set to 5°C. Increasing the reaction temperature up to 65°C led to the formation of polymer with 62% head-to-tail regioregulatiry (**P60**). **P60** had following apparent molecular weight parameters (polystyrene calibration): M_w = 7.2 kg mol^{-1}, M_n = 4.6 kg mol^{-1}, $Đ$ = 1.6. **P90** had following parameters: M_w = 13.2 kg mol^{-1}, M_n = 8.7 kg mol^{-1}, $Đ$ = 1.5.

The triethylphosphine reagent was added to a solution of polymer in toluene and then stirred under reflux for 24 h. Formed polyelectrolyte was twice precipitated from methanol/diethyl ether solvent system. It was subsequently washed by diethyl ether and then dried in vacuum to the constant weight. Polyelectrolyte sample possessing lower regioregularity and lower molecular weight is denoted as **P60-EtP$^+$** and the second conjugated polyelectrolyte with higher regioregularity and higher molecular weight is denoted as **P90-EtP$^+$**. Direct

determination of conjugated polyelectrolytes molecular weight using SEC is not possible due to strong interaction of the charged structures with the column system.

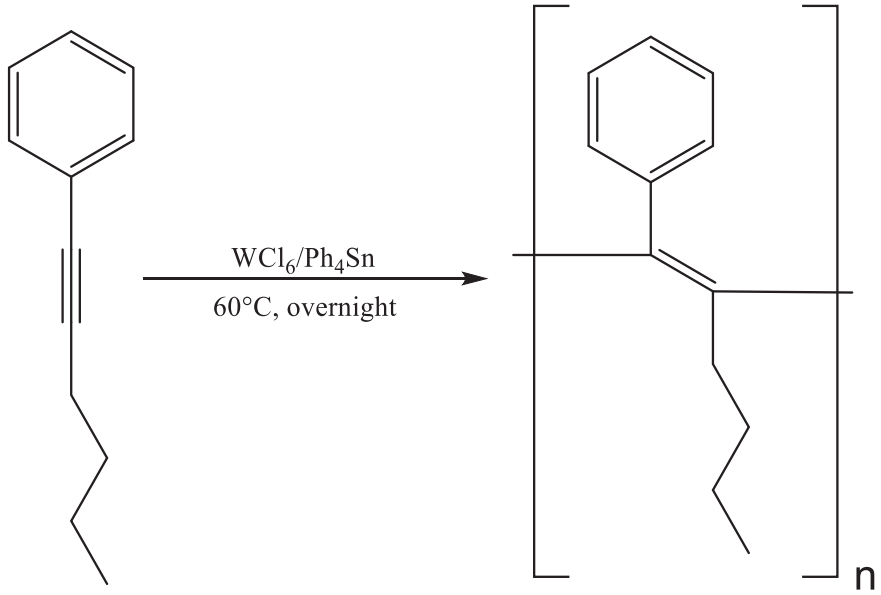


Scheme 7: Synthesis of poly {3-[6-(triethylphosphonium)hexyl]-thiophene-2,5-diyl bromide} via post-polymerization modification of polymer precursors **P60** and **P90**.

Polyacetylene – based material

Polymer poly(1-phenyl-1-hexyne) coded as **Br11** in further text was prepared according to the previously published procedure from the commercially available monomer (1-phenyl-1-hexyne) using $WOCl_4/Ph_4Sn$ metathesis catalytic system. All spectral characterizations are in a good accordance with previously published results[50,51]. The reaction is depicted in Scheme 8.

Polymer yield was 72%, apparent M_w = 7.5 kg mol^{-1}, M_n = 3.7 kg mol^{-1}, $Đ$ = 2.0 (polystyrene calibration).



Scheme 8: The polymerization of 1-phenylhexyne.

Fluorescence measurements of the conjugated polyelectrolytes P60-EtP$^+$ and P90-EtP$^+$

Investigation of quencher selectivity

In the current work the aqueous stock solutions of Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Cs^+ (all bearing perchlorate counterions, ClO_4^-) at constant concentration (10^{-4} mol·dm^{-3}) and constant volume (1 mL) were prepared. A prepared stock solution of **P60-EtP$^+$** in water (10^{-2} mol·dm^{-3} and 10 µL) was injected into the solution of particular salt previously prepared. Finally, the concentration of **P60-EtP$^+$** achieved the same value as concentration of metal ions used (10^{-4}mol·dm^{-3}) due to dilution (100 times). All samples were prepared at room temperature. The emission spectra of the resulting water solution of **P60-EtP$^+$** and its metal ion-based compositions were measured.

Estimation of detection limit

As mentioned in discussion, Ag^+ ions had enhanced selectivity among other used metals and therefore it was selected for determination of detection limit. Therefore, five stock solutions of the Ag^+ perchlorate salt at constant volume (1 mL) and various concentrations (from 10^{-8} mol·dm^{-3} to 10^{-4} mol·dm^{-3}) were prepared in water in order to find the concentration of detection limit.

Subsequently, the solution of **P60-EtP$^+$** at constant volume (10 µL) and constant concentration (10^{-2} mol·dm^{-3}) was added into each stock solutions of Ag^+ prepared and measured.

Photoluminescence quenching analysis of conjugated polyelectrolytes P60-EtP$^+$ and P90-EtP$^+$ by Stern-Volmer method

Ag^+ and Fe^{2+} metal ions were used as the luminescence quenching agents [*Q*] in order to study luminescence quenching of **P60-EtP$^+$** and **P90-EtP$^+$**. Different quencher's concentrations [*Q*] and constant concentration of polyelectrolytes synthesized were used for analysis (see Figures 4,5). The concentration of the polyelectrolytes was maintained constant throughout the whole experiment (10^{-4} mol·dm^{-3}, based on the monomer repeating units) in order to avoid possible concentration-dependent aggregation. The experiment was conducted in water at room temperature. The results were evaluated by Stern-Volmer methodology.

Fluorescence measurements of conjugated polymer Br11

The chloroform stock solution of **Br11** was prepared in the concentration of 10^{-5} mol dm^{-3} (based on the repeating unit). 3 mL of solution were transferred into the cuvette and 3 µL of nitrobenzene ($9.75 \cdot 10^{-2}$ mol·dm^{-3}) were added. Therefore, the resulting concentration of nitrobenzene in cuvette was $9.75 \cdot 10^{-5}$ mol·dm^{-3} due to the dilution (1000 times). The emission spectrum was measured and then 3 µL of nitrobenzene were added again to the same cuvette. The addition was done until the final volume of added nitrobenzene solution was 30 µL. All emission spectra are depicted in Figure 7. The experiment was conducted at room temperature. The results were evaluated by Stern-Volmer methodology.

4. Results and Discussion

4.1 Poly{3-[6-(triethylphosphonium) hexyl]-thiophene-2,5-diyl bromide}

Investigation of quencher selectivity

The emission measurements showed significant decrease in luminescence intensity for Ag^{+} metals. Moreover, Fe^{2+} and Co^{2+} metal ions showed also decrease in fluorescence intensity (see Figure 3). The sensitivity of **P60-EtP^{+}** (polymer sample with lower regioregularity) material towards other metals used exhibited negligible increase in luminescence intensity caused probably by a formation of strongly luminescent coordination species of phosphonium pedant groups with appropriate metal ions.

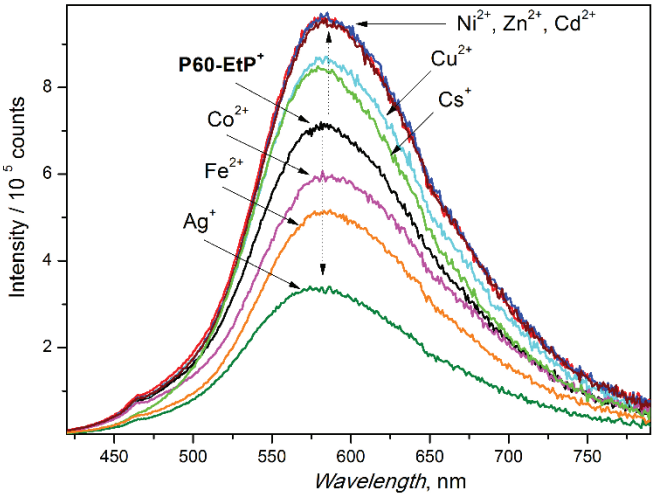


Figure 3: Emission spectra of **P60-EtP^{+}** (10^{-4} mol·dm^{-3}, based on polymer repeating unit) in the presence of different metal ions (10^{-4} mol·dm^{-3}) measured in water.

Estimation of detection limit

The fluorescence responses of polymer **P60-EtP^{+}** to the different concentrations of Ag^{+} metal ions were estimated by emission spectroscopy and their results are collected in Figure 4.

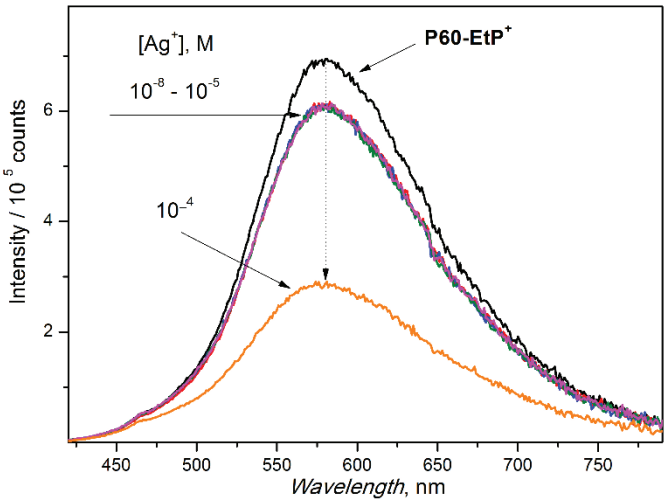


Figure 4: Photoluminescence spectra of **P60-EtP⁺** (10^{-4} mol·dm^{-3}, based on polymer repeating unit) with extended range of concentration of Ag^+ ions (10^{-8} – 10^{-4} mol·dm^{-3}) in water.

Figure 4 showed, that **P60-EtP⁺** exhibited detection range of concentration to Ag^+ metal ions till 10^{-4} mol·dm^{-3}. Lower concentrations. e.g. from 10^{-8} to 10^{-5} mol·dm^{-3} almost did not influence emission intensity. Therefore, concentration of metal ions around 10^{-4} mol·dm^{-3} was considered for more detailed analysis mainly of fluorescence quenching experiment described in experimental part.

Investigation of Stern – Volmer constants of selected quenchers

In this work, we showed the photoluminescence quenching of the prepared **P60-EtP⁺** and **P90-EtP⁺** in water using perchlorate salt of Ag^+ or Fe^{2+} as quenchers in concentration range from $6 \cdot 10^{-5}$ mol·dm^{-3} to $2 \cdot 10^{-4}$ mol·dm^{-3}. The results of this study were represented by Stern-Volmer constants (K_{SV}). The Stern-Volmer plots and photoluminescence quenching spectra of **P60-EtP⁺** and **P90-EtP⁺** polyelectrolytes are shown in Figures 5 and 6. Received Stern-Volmer constants are summarized in Table 1. Results showed that the luminescence quenching is more efficient for **P90-EtP⁺** polyelectrolyte than for **P60-EtP⁺** material. The values of K_{SV} for **P90-EtP⁺** are twice as much higher than values for **P60-EtP⁺**. This fact suggests that the higher regioregularity of polymer chains leads to improvement of sensing abilities of materials and can be used as a viable strategy for sensor's

development. Such improved properties of highly regioregular polyelectrolyte are caused by easy and rapid energy migration along more packed conjugated polymer main-chains in polythiophene. Moreover, Stern-Volmer constants for Ag^+ quencher are negligible higher than for Fe^{2+} metal ions indicating better detection abilities (see Table 1). Quencher concentrations and luminescence intensities used for Stern-Volmer constants are collected in Table 2.

Table 1: Summarized Stern-Volmer constants (10^3 mol^{-1}·dm^3)

Sample	K_{SV} (10^3 mol^{-1}·dm^3) / quenching agent	
	Ag^+	Fe^{2+}
P60-EtP⁺	5.2	3.7
P90-EtP⁺	8.9	8.6

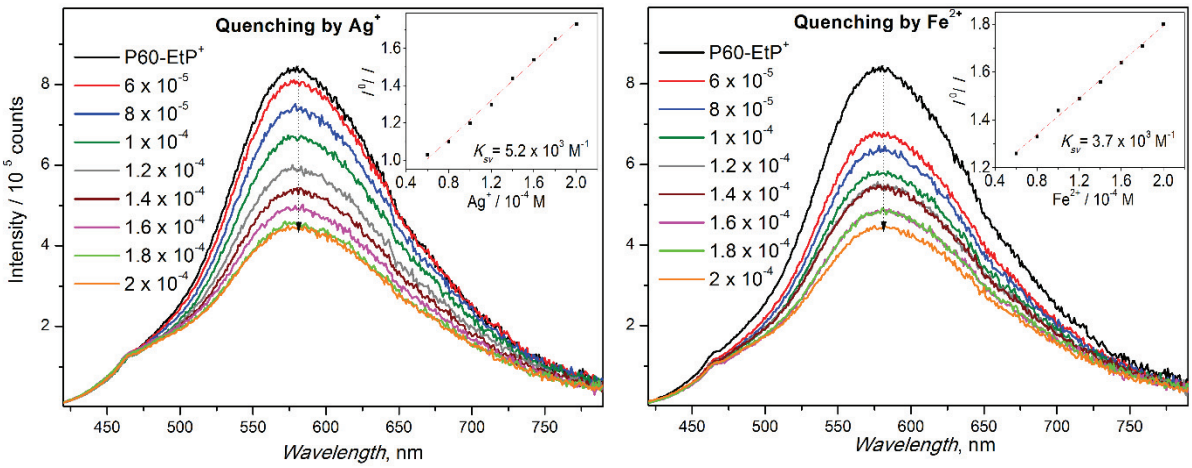


Figure 5: Photoluminescence quenching spectra of **P60-EtP⁺** polyelectrolyte by perchlorate salt of Ag^+ and Fe^{2+}. Inset: Stern-Volmer plots with indicated Stern-Volmer constants (K_{SV}), exited at λ_{exc} = 420 nm with constant slit width.

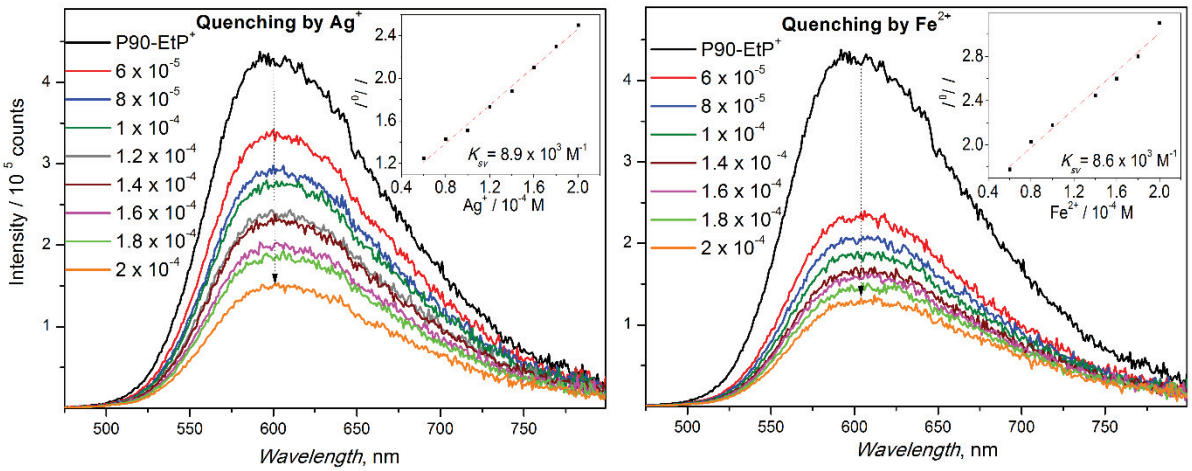


Figure 6: Photoluminescence quenching spectra of **P90-EtP⁺** polyelectrolyte by perchlorate salt of Ag^{+} and Fe^{2+}. Inset: Stern-Volmer plots with indicated Stern-Volmer constants (K_{SV}), exited at λ_{exc} = 420 nm with constant slit width.

Table 2: Results of luminescence quenching experiment of **P60-EtP⁺** and **P90-EtP⁺** conjugated polyelectrolytes by perchlorate salts of Fe^{2+} and Ag^{+} (used as quenchers). [*Q*] concentration of quencher, (mol·dm^{-3}); I^0/I ratio between integrated luminescence intensity with/without indicated quenching agent

P60-EtP⁺			**P90-EtP⁺**		
[*Q*]/ mol·*dm*$^{-3}$	I^0/I (Fe^{2+})	I^0/I (Ag^{+})	[*Q*]/ mol·*dm*$^{-3}$	I^0/I (Fe^{2+})	I^0/I (Ag^{+})
$6.0 \cdot 10^{-5}$	1.26	1.03	$6.0 \cdot 10^{-5}$	1.78	1.25
$8.0 \cdot 10^{-5}$	1.33	1.10	$8.0 \cdot 10^{-5}$	2.03	1.43
$1.0 \cdot 10^{-4}$	1.44	1.20	$1.0 \cdot 10^{-4}$	2.18	1.51
$1.2 \cdot 10^{-4}$	1.49	1.30	$1.2 \cdot 10^{-4}$	2.31	1.73
$1.4 \cdot 10^{-4}$	1.56	1.44	$1.4 \cdot 10^{-4}$	2.45	1.88
$1.6 \cdot 10^{-4}$	1.64	1.54	$1.6 \cdot 10^{-4}$	2.60	2.10
$1.8 \cdot 10^{-4}$	1.71	1.65	$1.8 \cdot 10^{-4}$	2.80	2.30
$2.0 \cdot 10^{-4}$	1.80	1.73	$2.0 \cdot 10^{-4}$	3.10	2.50

The second part of luminescence quenching study is devoted to comparison of quenching properties of the perchlorate salt of Fe^{2+} and $K_4[Fe(CN)_6]$ studied before in our laboratory[39]. It should be stressed, that quenching abilities of potassium ferrocyanide are exclusively based on complexation of used quencher[52]. Therefore, information about luminescence quenching of studied

conjugated polyelectrolytes by Fe^{2+} ions in different chemical components is valuable for further development and study of quenching agents as well as material's synthesis.

Comparison of two quenching agents bearing the same Fe^{2+} metal ions showed remarkable difference between them. The chosen quenching agent based on Fe^{2+} ions with perchlorate anions provided poor sensing abilities at low concentration. The efficient quenching was observed at concentration 10^{-4} mol·dm^{-3}. On the other hand, $K_4[Fe(CN)_6]$ quencher showed an opposite effect, where the efficient quenching was observed at concentration 10^{-7} mol·dm^{-3} and lower. This result confirmed difference in coordination species formed with Fe^{2+} metal ions in $K_4[Fe(CN)_6]$ and iron(II) perchlorate. Moreover, the values of Stern-Volmer constants for $K_4[Fe(CN)_6]$ are also higher than for perchlorate salt of Fe^{2+}.

However, quenching agent perchlorate salt of Ag^+ has never been studied before on such conjugated systems (**P60-EtP$^+$** or **P90-EtP$^+$**). It should be stressed that quenching of studied conjugated polyelectrolytes by Ag^+ was more efficient than by Fe^{2+}. As a result, chosen materials can be considered as promising materials for detection of Ag^+ in water.

4.2 Poly(1-phenyl-1-hexyne) (**Br11**)

We showed that poly(1-phenylhex-1-yne), **Br11** provided significant decrease in the fluorescence emission. It was characterised by a Stern-Volmer constant. The emission spectra and Stern-Volmer analysis is shown below in Figure 7.

In this work we showed quenching properties of prepared **Br11** (Poly(1-phenyle-1-hexyne)) in chloroform, with quenching agent nitrobenzene, which was never studied before with this polymer.

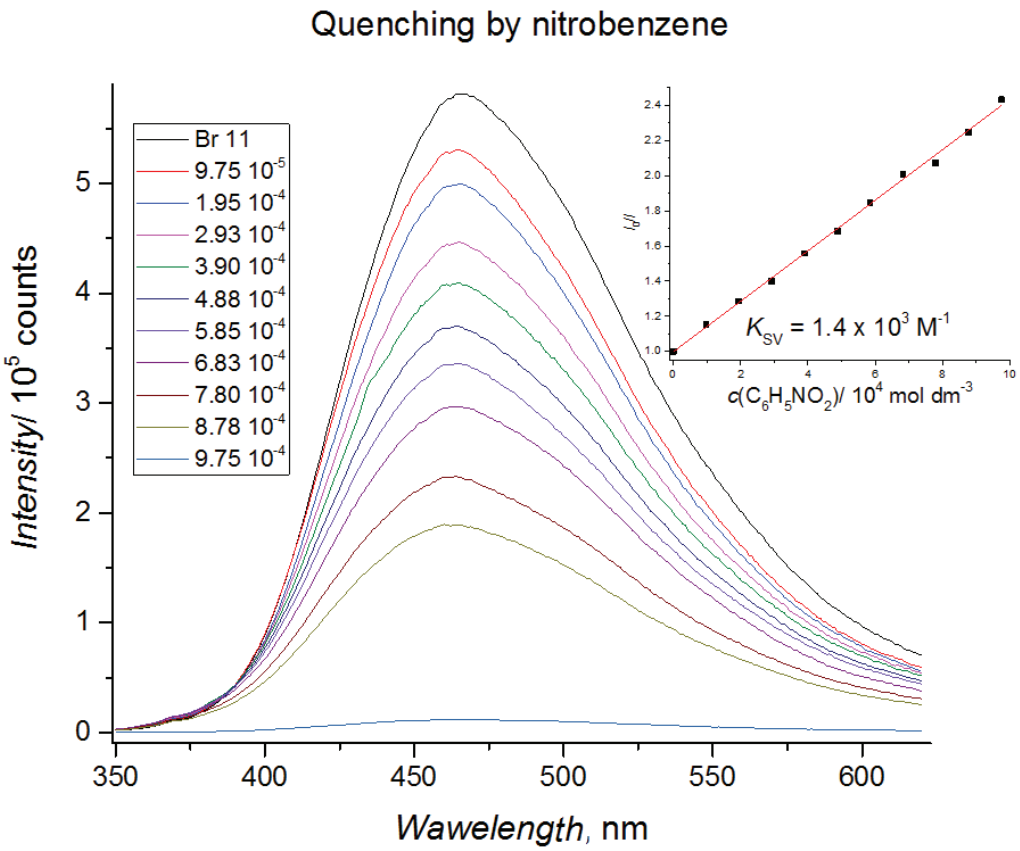


Figure 7:Course of *quenching of* photoluminescence **Br11** *upon quencher addition. Inset: Stern-Volmer plot with indicated Stern-Volmer constant* (K_{SV}).

The Stern-Volmer constant of quenching with nitrobenzene was estimated to $1.4 \cdot 10^3$ $mol^{-1}dm^3$. Fluorescence lifetime showed two-exponential decay (τ_1 = 0.6 ns with amplitude 45% and longer decay component τ_2 = 2.3 ns with amplitude 55%) – excited with laser diode (378 nm), emission monochromator was set to 450 nm. Mentioned decay was practically independent on quencher concentration. This observation may indicate a static quenching mechanism.

Table 3: Results of luminescence quenching experiment of **Br11** conjugated polymer by nitrobenzene (used as quenching agent), [*Q*], quencher's concentration, (mol·dm^{-3}); I^0/I ratio between integrated luminescence intensity with/without indicated quenching agent

$[Q]/10^{-4}$ mol·dm^{-3}	0.00	0.975	1.95	2.93	3.90	4.88	5.85	6.83	7.80	8.78	9.75
I_0/I	1.00	1.15	1.29	1.40	1.56	1.68	1.85	2.01	2.07	2.25	2.43

As shown in Figure 7, poly(1-phenyl-1-hexyne) can be used for detection of nitrobenzene from concentrations $9.75 \cdot 10^{-5}$ mol·dm^{-3} to $9.75 \cdot 10^{-4}$ mol·dm^{-3}. However, the polymer did not interact with any metal ions. Therefore, we presume, that introduction of halide (Cl, Br or I) followed by quaternization with phosphonium or ammonium – based group (PPh_3, PEt_3, etc.) will improve the sensing ability of polyacetylene based polyelectrolyte.

5. Conclusions

A line of Fe^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Cs^{+}, Co^{2+} and Ag^{+} perchlorates were used as with poly{3-[6-(triethylphosphonium) hexyl]-thiophene-2,5-diyl bromide} differing in main chain regioregularity (62 and 94%) in fluorescence quenching study. Only Ag^{+} and Fe^{2+} salts were found as effective quenchers. Luminescence quenching was evaluated by a Stern-Volmer methodology. We found that polyectrolyte with higher regioregularity is quenched twice as much effectively. Polyelectrolytes showed higher sensitivity to Ag^{+} than for Fe^{2+} ions. In addition we compared $Fe(ClO_4)_2$ and $K_4[Fe(CN)_6]$ quenchers. The comparison indicated more efficient luminescence quenching for $K_4[Fe(CN)_6]$. This observation indicates coordination mechanism of quenching where coordination style plays an important role in quenching process.

Moreover, poly(1-phenyl-1-hexyne) was synthesized as a model polymer using metathesis polymerization. Luminescence of mentioned polyacetylene based polymer was efficiently quenched by nitrobenzene. Independence of luminescence decay on quencher concentration may indicate a static luminescence quenching mechanism. Poly(1-phenyl-1-hexyne) luminescence is not sensitive to any metal-ion-based quencher.

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